

PATENT SPECIFICATION

NO DRAWINGS

994769

Date of Application and filing Complete Specification: March 25, 1964.

No. 12641/64.

Application made in United States of America (No. 269,181) on March 29, 1963.

Application made in United States of America (No. 351,506) on March 12, 1964.

Complete Specification Published: June 10, 1965.

© Crown Copyright 1965.



Index at acceptance:—O2 C(3A10B2C, 3A10B5C)

Int. Cl.:—C 07 c

ВЕСОЮСНА.
ПАТЕНТНО-
ТЕХНИЧЕСКАЯ
БИБЛИОТЕКА

COMPLETE SPECIFICATION

Purification of Terephthalic Acid

We, STANDARD OIL COMPANY, a corporation organized and existing under the laws of the State of Indiana, United States of America, of 910, South Michigan Avenue, Chicago 80, Illinois, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the purification of terephthalic acid, and more particularly concerns the preparation of terephthalic acid having a purity sufficient for direct esterification with glycols to produce super polyesters.

High molecular weight polyesters of terephthalic acid with various glycols find extensive use as fibres, e.g. under the Trade Marks Dacron and Terylene and as film, e.g. under the Trade Mark Mylar. These super polyesters have heretofore been prepared from dimethylterephthalate, which is trans-esterified with the appropriate glycol and then polycondensed to form the super polyester. Polyester preparation via dimethylterephthalate has been considered an essential step by reason of the exceptionally high purity requirements imposed on the polyester.

Recently, with the advent of improved processes for the manufacture of terephthalic acid, much attention has been directed to the possibility of obtaining polyesters by direct esterification of terephthalic acid with the glycol. This would have manifest advantages of simplicity and economy as compared with the dimethylterephthalate route. As yet, however, there remains serious difficulty in obtaining terephthalic acid of suitable purity. Unless the initial terephthalic acid is virtually completely free from extraneous contaminants, the polyester will have too low a melting point and will be of unsatisfactory colour.

It is believed that terephthalic acid impurities are of two types. First, the compound 4-carboxybenzaldehyde, an intermediate formed

when terephthalic acid is obtained from the oxidation of paraxylene or a similar dialkyl benzene, is known to be deleterious with respect to polyester quality. Second, unidentified colour bodies, possibly of the benzyl or fluorenone structure, are usually present as trace by-products of most terephthalic acid production processes, and yield off-colour polyesters. Any method of purifying terephthalic acid must reduce or eliminate both the 4-carboxybenzaldehyde and the colour bodies.

It has now been found that terephthalic acid of a purity suitable for direct esterification with glycols to produce films and fibres may be obtained from impure terephthalic acid containing 4-carboxybenzaldehyde and other impurities by catalytically hydrogenating the impure terephthalic acid in an aqueous liquid phase solution at elevated temperature and pressure. By this process, there is a chemical reduction of the 4-carboxybenzaldehyde as well as a significant destruction of the colour body impurity.

The invention thus comprises a process for producing fibre-grade terephthalic acid from an impure terephthalic acid containing 4-carboxybenzaldehyde and other impurities, which process comprises catalytically hydrogenating said impure terephthalic acid in an aqueous solution at elevated temperature and pressure for a time sufficient to effect substantial reduction of said 4-carboxybenzaldehyde, and recovering a terephthalic acid of fibre-grade quality containing substantially less of said 4-carboxybenzaldehyde and other impurities.

Terephthalic acid obtained by the process of the invention is said to be "fibre-grade" quality. The term "fibre-grade" does not denote a quantitative degree of purity, but rather describes a terephthalic acid which is sufficiently free from 4-carboxybenzaldehyde and other impurities so as to yield a super polyester by direct esterification with a glycol which is satisfactory for the intended purpose.

[Price 4s. 6d.]

Thus, terephthalic acid polyester intended for transparent film or white fibre will require significantly higher purity terephthalic acid than polyesters intended for tire reinforcing cord. A tentative approximation of maximum 4-carboxybenzaldehyde content of terephthalic acid for colourless film and fibre is only about 50 parts per million, while for tire cord it may be as high as 500 parts per million or even higher.

4-Carboxybenzaldehyde is on occasion hereinafter referred to as 4-CBA.

Impure terephthalic acid which may be treated by the process of the invention may be obtained from any source. Excellent results have been shown when the terephthalic acid is produced by the liquid phase air (molecular oxygen) oxidation of paraxylene using a heavy metal and bromine as catalyst (Patent Specification No. 807091), although terephthalic acid from other of the catalytic liquid phase oxidations of p-xylene with molecular oxygen in the presence of heavy metal oxidation catalyst such as those promoted with acetaldehyde or methyl ethyl ketone, for the terephthalic acids recovered from these oxidation processes also contain 4-CBA impurity. The terephthalic acid from the nitric acid oxidation of paraxylene has been reported as containing 4-CBA impurity. Terephthalic acid from the isomerization of dipotassium orthophthalate, or the disproportionation of potassium benzoate, if carboxybenzaldehyde or reducible impurities are present, may similarly be benefitted by the process of this invention. By employing the inventive process, terephthalic acid from any source containing as much as two or three weight percent 4-carboxybenzaldehyde and which is yellowish in colour, can be converted to fibre-grade terephthalic acid by the process of this invention.

The process of the invention is conducted at elevated temperature and pressure with the terephthalic acid dissolved in an aqueous solvent. By reason of its low solubility terephthalic acid requires either large volumes of water or high temperature in order to obtain the desired terephthalic acid solution. For reasons of economic equipment design and process operation, it is therefore desirable to conduct the process within the range of about 200 to about 400°C., although lower or high temperatures may be used in particular circumstances. The most advantageous temperature range appears to be about 225—275°C., e.g. 240—260°C. The quantity of water needed to dissolve the terephthalic acid at various temperatures may be estimated from the table below:

Terephthalic Acid g./100 g. H ₂ O	Temperature, °C. for solution
1	185
5	225
10	242
20	259
50	272

Pressure conditions for the process of the invention depend upon the manner in which the process is conducted. Since the temperatures at which the impure terephthalic acid is dissolved in water are advantageously substantially above the boiling point of water and since the process of the invention is to be carried out in a manner to maintain a liquid phase of the aqueous solution, the process is necessarily carried out at a pressure above atmospheric pressure. When the process is carried out by batch treatment of individual batches of aqueous solutions of impure terephthalic acid under static conditions as in a sealed autoclave, higher hydrogen partial pressures are required to provide the hydrogen driving force are required to dissolve the hydrogen and permit it to diffuse to and reach the reducible dissolved impurity, than are required for dynamic conditions whereby hydrogen is intimately dispersed throughout the solution as by vigorous stirring, by introducing hydrogen streams into the aqueous solution, by bubbling hydrogen uniformly into the aqueous solution or by other dynamic means for providing intimate contact by hydrogen into the solution. These more dynamic means for providing intimate contact between hydrogen and the aqueous solution result in lower driving forces necessary for the hydrogen to reach the dissolved reducible impurities. Much lower hydrogen partial pressures or hydrogen driving forces are required where the aqueous solution of the impure terephthalic acid is percolated through a bed of hydrogenation catalyst and either a static hydrogen atmosphere or a flow concurrent or countercurrent of hydrogen through the catalyst chamber is maintained. These lower hydrogen partial pressures for the aforementioned percolation method of conducting the process of the invention provide a thin film of aqueous solution of the impure terephthalic acid on the catalyst particles and thus a rather low hydrogen driving force is needed for the hydrogen to dissolve and diffuse through the thin liquid layer and reach the catalyst. For such a percolation method of conducting the process a continuous flow or atmosphere of hydrogen is not essential. For example, the benefits of the percolation method can be obtained for a substantial period of time by

percolating the aqueous solution of impure terephthalic acid over a hydrogenation catalyst extended on a porous support which has been saturated with adsorbed hydrogen. The adsorption of hydrogen by the porous support can be accomplished before contacting the extended catalyst with the impure aqueous solution of terephthalic acid or it can be accomplished while contacting the extended catalyst with the impure aqueous solution of terephthalic acid. Thus, the process of this invention can be practiced by intermittent introduction of hydrogen into the bed of extended catalyst during the continuous introduction of the aqueous solution of impure terephthalic acid. The minimum of hydrogen to be introduced intermittently is, of course, an amount of hydrogen in excess of that required for reduction of the dissolved impurity so that adsorption of the excess hydrogen in the porous catalyst support can be simultaneously accomplished. When utilizing the foregoing method of conducting the process taking advantage of the hydrogen absorbed by the porous support of the extended catalyst, the actual partial pressure of hydrogen in the system is immeasurably low.

Very little hydrogen is consumed by the purification process of this invention. It appears that in the dynamic methods, dynamic with respect to hydrogen, of conducting the process of this invention, e.g. the aforementioned percolation method as well as the batch methods wherein hydrogen is mechanically, uniformly and intimately dispersed throughout the aqueous solution of impure terephthalic acid, measurably low partial pressures of hydrogen, e.g. 1 to 3 pounds per square inch absolute (p.s.i.a.) will permit obtaining the benefits of the process of the invention.

It is also advantageous in conducting the process of the invention, especially for the methods involving flow contact of the aqueous solution with hydrogenation catalyst, to impose on the aqueous solution being treated a pressure above the steam pressure required to maintain a liquid phase of the aqueous solution of impure terephthalic acid. This can be readily accomplished by use of an inert gas such as nitrogen. By "inert" gas is meant a gas which is inert to terephthalic acid as well as to the hydrogen. Nitrogen is an excellent inert gas. Also, the use of nitrogen permits the dilution of hydrogen to be introduced into the process and thereby provides low partial pressures of hydrogen.

In summary of the foregoing with respect to the use of hydrogen in the process of the invention, the hydrogen partial pressure can vary in the range of from as little as the aforementioned immeasurable low hydrogen partial pressure (hydrogen adsorbed on the porous support of extended catalyst) to one atmosphere (14.7 p.s.i.a.) for a percolation system and up to as much as 100 atmospheres

or more for the static batch method of conducting the process of this invention. It will be appreciated that the hydrogen driving force can be so great as to produce severe hydrogenation causing for example the conversion of 4-CBA to para-toluic acid or further to p-xylene and products between p-toluic and p-xylene as well as causing nuclear hydrogenation of the benzene ring of terephthalic acid thereby converting some of the terephthalic acid to hexahydroterephthalic acid (cyclohexane 1,4-dicarboxylic acid). Such severe hydrogenation producing side reactions do not negate the efficacy of the 4-CBA removal from the impure terephthalic acid. However, such severe hydrogenations should be avoided to prevent the conversion of terephthalic acid to some other product such as cyclohexane 1,4-carboxylic acid and to minimize the conversion of 4-CBA to p-toluic acid. It appears that the reduction of 4-CBA to methylol benzoic acid in the process of this invention is preferred over the reduction of 4-CBA to p-toluic acid because the methylol benzoic acid is more readily retained in the aqueous solution than is p-toluic acid when crystallizing terephthalic acid from aqueous solution which has been treated by the process of the invention. There are known methods for removing p-toluic acid from terephthalic acid but to employ these known methods would require an additional process step. Because cyclohexane 1,4-dicarboxylic acid differs sufficiently from terephthalic acid in physical properties, the removal of cyclohexane dicarboxylic acid from terephthalic acid can be accomplished but here, again, additional processing steps are required. The principle objective as hereinbefore stated is to obtain a terephthalic acid product of sufficiently high purity, therefore, exceptionally low impurity content, so that the purified terephthalic acid is suitable for direct esterification with glycols and subjection thereafter to polyesterification techniques to produce terephthalic acid polyesters of acceptable physical properties; that is, the objective is to produce a Fibre-grade terephthalic acid. Using too severe hydrogenation, although removing the 4-CBA impurity, would add additional different impurities which may be undesirable for the aforementioned direct reaction followed by polyesterification.

Treating time will depend on the initial terephthalic acid purity (that is, the amount of impurity to be reduced), on the desired Fibre-grade specifications imposed on the purified terephthalic acid and on other conditions of the hydrogenation, such as, for example, catalyst activity. Ordinarily a treating time (contact time) within the range of about 0.005 to about 10 hours, advantageously about 0.01 to 2 hours, will suffice for most operations. Although treating time is not a critical variable

it must be taken into consideration with regard to the aforementioned severe hydrogenation and to its side effects. Prolonging the time of treatment especially for the static batch methods of conducting the process, keeping in mind the aforementioned effects of severe hydrogenation conditions, increases the degree of throughput purification. However, on the more efficient hydrogenations such as the dynamic batch and flow methods of conducting the process, prolonging the time of treatment can result in too severe hydrogenation.

Conditions for conducting the process of the invention can be readily ascertained with respect to adequate vis-à-vis too severe hydrogenation by simple tests under the conditions selected to be employed with the particular method of conducting the process. For example, by conducting these simple bench-scale tests there can readily be determined contact time in a flow system, hydrogen partial pressure for a static batch system, and hydrogen driving force for the flow system, which enhance the formation of p-toluic acid and/or cyclohexane 1,4-dicarboxylic acid to a point beyond which these side products are retained in water under the conditions of crystallizing purified terephthalic acid from the aqueous solution resulting from the process. In general, the static batch method of conducting the process results in little excess formation of p-toluic acid and substantially no cyclohexane 1,4-dicarboxylic acid, even when exceptionally high hydrogenation driving forces, hydrogen partial pressures, are employed. Even the vigorous agitation of the slurry of catalyst and batch aqueous solution of impure terephthalic acid with dispersed hydrogen at high hydrogen partial pressures appear seldom to provide the too severe hydrogenation hereinbefore discussed. Hydrogenation severities which convert 4-CBA all the way to p-xylene are not disadvantageous to the direct esterification polycondensation because the p-xylene side product is non-reactive in those reaction systems.

A hydrogenation catalyst is required for the process so as to convert the aldehyde carbonyl group on the 4-carboxybenzaldehyde at least to a methylol group, e.g. p-methylol benzoic acid, and to destroy, or otherwise render innocuous, other impurities present in the feed terephthalic acid. A wide variety of catalysts has been found efficacious, and while carbon-supported noble metals are outstanding, reference may be made to any of the standard texts on hydrogenation or catalysts for alternative materials which are catalytically effective under aqueous phase hydrogenation conditions. Numerous catalysts are listed, for example, in Kirk and Othmer's "Encyclopedia of Chemical Technology" (Interscience), particularly the chapters on Hydrogenation and Catalysts; Emmett's "Catalysis", (Reinhold), particularly

Volumes IV and V on Hydrogenation; Lohse's "Catalytic Chemistry", (Chemical Publishing Company), particularly the sections on Group VIII Metal Catalysts. Illustrative catalysts include the Group VIII Noble Metals Ruthenium, Rhodium, Palladium, Osmium, Iridium, and Platinum, advantageously extended on a support such as activated carbon; the other Group VIII metals, iron, cobalt, and nickel, in the form of their finely divided elemental metals or their salts such as the nitrates; Raney nickel; platinum or palladium black; palladium chloride or nitrate; nickel metal on Kieselguhr. It appears that the supported noble metals are particularly outstanding with respect to hydrogenating 4-carboxybenzaldehyde while the iron-cobalt-nickel elements and compounds are excellent in removing coloured impurities, and accordingly mixtures of a noble metal and iron-cobalt-nickel elements or compounds are exceptionally useful.

The quantity of catalyst will depend, as will other facts, on the desired extent of purification and on the activity of the catalyst. These inter-relationships, however, are best determined by simple experimentation on a laboratory or pilot plant scale, suitably with reference to the examples furnished below.

To illustrate various embodiments of the invention, the following examples are presented. These are intended for illustrative purposes only and are not to be considered wholly definitive or exclusive with respect to scope and conditions. In each example, the 4-carboxybenzaldehyde content was determined by dissolving the terephthalic acid in dilute alkali and buffering to a pH of 9, followed by polarographic analysis to determine "4-CBA" content. Colour, expressed as "T.E.G. Colour" (triethylene glycol colour) was determined by esterifying 4.0 grams of the terephthalic acid with 28.4 cc of triethylene glycol at 260 degrees C., followed by comparing the resultant solution colour with American Public Health Association (APHA) standards.

EXAMPLES

Except as otherwise specifically noted, all of the following examples are conducted by admixing the designated quantities of catalyst, terephthalic acid, and water at room temperature in a pressure vessel equipped with means for agitating its contents. Hydrogen gas is introduced to the designated pressure, the vessel sealed, and the contents heated to the specified temperature and maintained at that level for the indicated time. Thereafter, the vessel is permitted to cool slowly to room temperature (where a solid catalyst is employed this catalyst is filtered out at reaction temperature prior to cooling), and the purified terephthalic acid filtered off. Triethylene glycol colour and 4-carboxybenzaldehyde content are determined on the filtered product.

TABLE I
Hydrogenation of Aqueous Terephthalic Acid Solutions
Hydrogenation Conditions ()

Example	Catalyst	Catalyst, Grams	Terephthalic Acid, G.	Water, CC's.	Temp., °C.	H ₂ Press., PSIG., Cold	Time, Min.	Filtration, °C. (c)	T.E.G. Colour	4-CBA Wt. %
0	None								430	0.128
1	65% Ni on Kieselguhr	0.1	30	350	243	130/120	60	22		0.006
2	5% Pd. on C. Powder (a)	0.133	30	350	243	100/90	90	22	80 (f)	0.0009
3	5% Pd. on C. Powder (a)	0.25	100	1000	246	100/—	60	22 (d)	340	0.002
4	0.5% Pd. on C. Powder	4.0	100	1000	246	100/—	120	22	185	0.003
5	0.2% Pd. on 4—8 Mesh C. (b)	1.0	100	1000	246	100/—	60	22	140	0.088
6	0.1% Pd. on C. (b)	4.0	100	1000	246	100/—	120	22 (e)	350	0.003
7	5% Pd. on C. Powder (b)	0.1	30	350	246	105/105	95	22	300	0.0020
8	Co (NO ₃) ₂	0.1	30	350	246	100/100	60	22	240	0.068
9	Co (NO ₃) ₂	0.4	100	1000	246	100/—	60	160 (h)	80	0.024
10	Pd (NO ₃) ₂	0.01	30	350	246	100/90	5	22	130	0.029
11	Pd Cl ₂	0.0616	30	350	243	100/90	60	22	40	<5 ppm

(a) Matheson, Coleman & Bell.

(b) Engelhard.

(c) Cooled slowly, unless otherwise specified.

(d) 30 Min. to 201°, rapidly to 22°.

(e) 50 Min. to 201°, rapidly, to 22°.

(f) After acid wash to remove catalyst

(g) Catalyst not filtered from solution. Product was dissolved in caustic, then filtered to remove catalyst, sprung with HCl and washed with 30 vol./vol. water.

(h) Runs with 350 cc. water are in 830 ml. S.S. Recker Bomb; other Runs are in 1-gallon Magnedrive Bomb.

In the following illustrative Examples 12 through 23 a percolation method of conducting the process of the invention is employed. In this percolation method 0.5% by weight palladium on 4-8 mesh granular carbon is employed as the hydrogenation catalyst. The catalyst is wet screened through a 10 mesh screen (hole size 0.62 inch.) Of the wet screened catalyst 8.44 pounds are added to a tubular titanium column having an internal diameter of 4 inches. The length of the resulting catalyst bed is 44 inches. The catalyst is supported on a titanium plate screen having holes of 0.043 inch diameter on 0.078125 inch centres. An aqueous solution of impure terephthalic acid is percolated through the column with the solution of impure terephthalic acid entering the top of the column and the treated solution being withdrawn from the bottom of the column. Hydrogen or hydrogen-containing gas, when used, is added at the top of the column and, therefore, the hydrogen is used in concurrent flow. The treated solution flowing from the column is, of course, collected under pressure and thereafter cooled and depressurized to crystallize therefrom dissolved terephthalic acid. The crystallized terephthalic acid is recovered by filtration and is washed and dried. The purity of the washed and dried terephthalic acid is determined.

The impure terephthalic acid employed for Example 12 contains 6100 parts per million (ppm) 4-CBA, 180 ppm benzoic acid and 1300 ppm p-toluic acid. The TEG colour of this impure terephthalic acid is 230 and the impure terephthalic acid has an optical density at 380 m μ of 0.31 and at 340 m μ of 1.08.

The impure terephthalic acid employed for Examples 13 through 22 has 4070 ppm 4-CBA. The impure terephthalic acid used for Example 23 has 4000 ppm 4-CBA.

The weight percent of dissolved solids, the temperature, pressure, and space velocity of the aqueous solution of the various impure terephthalic acids are shown in Table II. The theoretical amount of hydrogen to convert 4-CBA to p-methylol benzoic acid is one

mol of hydrogen per mol of 4-CBA. There is also shown in Table II the hydrogen partial pressure employed and the resulting mol ratio of hydrogen to 4-CBA.

With respect to the data in Table II there is shown the 4-CBA content of the recovered, washed, and dried purified terephthalic acid in parts per million of 4-CBA and the TEG Colour and optical density of the purified terephthalic acid. Also shown when determined are the parts per million of benzoic acid, p-toluic acid, p-methylol benzoic acid and cyclohexane 1,4-dicarboxylic acid content of the purified terephthalic acid. All of these compounds are shown in parts per million.

Examples 14 through 22 were run consecutively and, as will be noted, hydrogen feed was introduced only in Examples 14, 15, and 22. These examples illustrate the aforementioned intermittent addition of hydrogen as well as the reduction of 4-CBA by hydrogen adsorbed by the catalyst support. Examples 22 and 23 also illustrate the use of hydrogen diluted with nitrogen.

In Examples 15 and 17 through 21 where no hydrogen feed is used the most likely source of hydrogen is the hydrogen adsorbed by the catalyst support during previous purification. Since Examples 17 through 21 processed 98 pounds of terephthalic acid containing 4070 ppm 4-CBA through the catalyst, it is not stretching credulity to adsorb the theoretical amount of hydrogen necessary for the reduction of 4-CBA. More important from a kinetic standpoint, there was sufficient hydrogen adsorbed during the earlier treating procedure to purify at least ten times the catalyst weight of terephthalic acid after stopping the addition of hydrogen. This is indicative of the large hydrogen excess available of the excessive mass transfer rate of the hydrogen to the catalyst over that needed for the 4-CBA reduction. Substantiating this is the ring attack by hydrogen in the previous percolation treatments where hydrogen was introduced into the column resulting in the formation of cyclohexane 1,4-dicarboxylic acid.

TABLE II

Example No.	12	13	14	15	16	17	18	19	20	21	22	23
4-CBA in Feed TA (%) ppm	6100	4070	4070	4070	4070	4070	4070	4070	4070	4070	4070	4000
Feed Solution:												
Dissolved Solids Wt. %	10.0	8.63	12.9	7.81	8.5	7.08	8.01	8.28	10.17	10.21	10.85	9.38
Temperature °C.	246	249	260	249	249	251	251	251	251	251	249	249
Pressure psig.	645	570	690	580	580	570	570	575	575	580	570	580
Space Velocity (°) lb/hr/ft ³	32.6	32.6	39.4	37.0	34.2	35.0	35.1	35.4	38.5	36.6	39.6	37.1
Mol ratio H ₂ /4-CBA	335	159	91	(3)	646	(3)	(3)	(3)	(3)	(3)	18.0 ⁽⁹⁾	16.6
Hydrogen Pressure psia	120	19	24	(3)	29	(3)	(3)	(3)	(3)	(3)	2.83	9.0 ⁽⁹⁾
Recovered Terephthalic Acid:												
4-CBA ppm	5	5	10	7	20	17	10	<10	80	58	26	<10
TEG Colour APHA	75	70	94	54	112	44	6	12	10	42	14	15
Optical Density 380 mμ	0.085	0.035	0.026	0.015	0.050	0.027	0.006	0.006	0.013	0.031	0.012	0.009
Optical Density 340 mμ	0.114	0.054	0.036	0.026	0.078	0.056	0.024	0.106	0.055	0.081	0.027	0.024
Benzoic Acid ppm	—	40	<10	N.D. ⁽⁶⁾	29	85	67	52	21	43	<10	<10
p-Toluic Acid ppm	—	3300	2300	49	1600	1200	840	180	620	450	460	180
Methylol Acid (°) ppm	—	N.D.	N.D.	94	65	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	—
1,4-CHDCA (°) ppm	—	33	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	—

(1) p-Methylol benzoic acid

(2) Cyclohexane-1,4-dicarboxylic acid

(3) No hydrogen feed

(4) 14.1 mol % H₂ mixture with nitrogen(5) In Example No. 23 30 mol % H₂ mixture with nitrogen

(6) N.D. is none detected

(7) Space velocity is in pounds of solution per hour per cubic foot of catalyst bed

(8) TA is terephthalic acid

EXAMPLE 24

A percolation column of titanium similar to that hereinbefore described but having an internal diameter of only one inch and containing 325 grams of catalyst (0.5% Pd. on charcoal) is employed. To this column there is fed an aqueous solution of impure terephthalic acid containing 10 pounds of impure terephthalic acid per 100 pounds of water. The impure terephthalic acid contains 1.0 weight percent 4-CBA (10,000 ppm). The operating temperature is 249°C. and the total pressure is 670 p.s.i.g. The hot pressurized solution is fed into the top of the catalyst bed. Also hydrogen diluted with nitrogen is fed into the top of the bed as before. In this example the hydrogen partial pressure is 10 p.s.i.a. The space velocity of the solution is 587.5 pounds of solution per hour per cubic foot of catalyst bed. The mol. ratio of hydrogen to 4-CBA is 4. The contact time in the percolation column is 48 seconds. By this percolation method there is obtained a washed and dried terephthalic acid having a 4-CBA content of less than 10 parts per million.

It is evident from the above that the process of the invention is capable of producing exceptionally high quality terephthalic acid, capable of meeting even the most stringent requirements of fibre-grade material.

While the invention has been described in conjunction with specific embodiments, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. For example, instead of slurrying the solution of terephthalic acid with catalyst under hydrogen pressure in an agitated reaction vessel, hydrogen gas may be bubbled upward through the slurry or solution. Alternatively, and of particular significance in view of the almost insignificant hydrogen consumption, a fixed bed of catalyst may be provided and maintained under stagnant hydrogen pressure while the aqueous terephthalic acid solution is permitted to percolate downward through the catalyst bed; this minimizes or avoids the need for recycling or compressing the hydrogen gas.

Furthermore, and as suggested by the results of Example 9, it is advantageous to filter or otherwise separate the terephthalic acid from the mother liquor at a somewhat elevated temperature, e.g. about 50—150, or optimally about 80—120°C., so as to retain a more substantial quantity of coloured impurities in solution and to exclude them from the purified terephthalic acid crystals.

Also, under particular circumstances, it may be desirable to recover the terephthalic acid by evaporating or flashing off the water, rather than by cooling and separating the solid terephthalic acid. In this event, washing the terephthalic acid with dilute aqueous hydrochloric or other mineral acid to remove last traces of catalyst (where a catalyst other than a noble

metal is employed) may be of advantage.

One of the outstanding features of the process of the invention is that it can be conducted under conditions such that there is essentially no hydrogenation of the benzene ring. For example, in Example 1, the product was analyzed for the presence of hexahydroterephthalic acid and it was found that this was below the limit of detection, i.e., below 0.005 weight percent.

It is therefore apparent that the process of the invention is capable of producing fibre-grade terephthalic acid to the highest purity specifications.

WHAT WE CLAIM IS:—

1. A process for producing fibre-grade terephthalic acid from an impure terephthalic acid containing 4-carboxybenzaldehyde and other impurities, which process comprises catalytically hydrogenating said impure terephthalic acid in an aqueous solution at elevated temperature and pressure for a time sufficient to effect substantial reduction of said 4-carboxybenzaldehyde, and recovering a terephthalic acid of fibre-grade quality containing substantially less of said 4-carboxybenzaldehyde and other impurities.

2. A process according to Claim 1 wherein said hydrogenation is effected at a temperature of from 200 to 400°C. and for a time of from 0.005 to 10 hours.

3. A process according to Claim 1 or 2 wherein said fibre-grade terephthalic acid is recovered by cooling said solution and separating terephthalic acid crystals from the mother liquor.

4. A process according to Claim 1, 2 or 3 wherein said hydrogenation catalyst is a solid material, and is separated from said solution prior to recovering said terephthalic acid.

5. A process according to any of the preceding Claims wherein said hydrogenation catalyst is a noble metal extended on a carbon support.

6. A process according to Claim 5 wherein said noble metal is platinum.

7. A process according to Claim 5 wherein said noble metal is palladium.

8. A process according to any of Claims 1 to 4 wherein said hydrogenation catalyst is nickel on kieselguhr.

9. A process according to any of Claims 1 to 7 wherein said aqueous solution is percolated through a bed of noble metal extended on a carbon support.

10. A process according to Claim 9 wherein hydrogen is introduced continuously with said aqueous solution.

11. A process according to any of Claims 1 to 4 wherein said hydrogenation catalyst comprises a noble metal and iron, cobalt or nickel.

12. A process as claimed in Claim 1 substantially as hereinbefore described and exemplified.

13. Terephthalic acid when purified by the

process claimed in any one of the preceding
Claims.

MATHYS & SQUIRE,
Chartered Patent Agents,
Staple House, 51/52, Chancery Lane,
London, W.C.2.
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press
(Leamington) Ltd.—1965. Published by The Patent Office, 25 Southampton Buildings,
London, W.C.2, from which copies may be obtained.